SYNTHESIS OF HIGH SURFACE BAO NANOPARTICLES USING SOLAR ENERGY

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PETRONAS

Synthesis of High Surface CdO Nanoparticles Using Sol-Gel Method

By,

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Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JULY 2009

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ABSTRACT

The main objective of this study is to synthesis high surface of CdO nanoparticles using sol-gel method. After that the synthesized product will be characterized using several equipments. Scope of worked is focused in the synthesizing parameters as well as to study the morphology of the final product after calcinations process. The synthesizing process involves in several parameters that affect the final product of CdO. This parameters need to be control in order to get the anatase paste CdO with high surface area. Slightly change in some parameters will lead to failure of product. Some parameters that will be considered are the calcinations temperature. The calcinations temperature will be isolated in order to get the best product. For better formation of during for the process TEOS is used by the author. TEOS need to be hydrolysis with ethanol initially and added the solution of Cadmium Sulphate and distilled water. Since the precursor of the synthesis is from Cadmium Sulphate and will be added with acid to form sol. As for the methodology, the general experimentation is addition of Cadmium Sulphate with Nitric Acid and distilled water. After left at ambient temperature for about 2 hours, then NaOH is added to the solution. Then filter and wash of the initial product then put in oven to remove water. Before calcinations TGA need to be done. Finally after calcinations, the product should be characterized. Then the objectives will be determined whether achieve or not.

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Synthesis of High Surface CdO Nanoparticles Using Sol-Gel Method

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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

_____

(Assoc. Prof. Dr Anita bt Ramli)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

JULY 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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MOHD NOOR BIN ZAKARIA

ACKNOWLEDGEMENT

First and foremost, our utmost thanks and gratitude to Allah Subhanahu Wa Taala for bestowing the great needed strength, audacity and knowledge in completing this project.

The author would like to acknowledge and extend our heartfelt gratitude and appreciation to the supervisor AP Dr Anita bt Ramli, Allah Almighty has made it possible for this research to complete. Her support, guidance and encouragement throughout the duration of this study are sincerely acknowledged.

Ultimately but most essentially the author would like to thank all those who have contributed towards making this project success both direct and indirect. To colleagues, other students, friends and members of our family who have helped extend our involvement in this project.

Many thanks to all.

CHAPTER 1
INTRODUCTION

1.1 PROJECT WORK BACKGROUND

The sol-gel process is a versatile solution process for making ceramic and glass materials. In general, the sol-gel process involves the transition of a system from a liquid "sol" (mostly colloidal) into a solid "gel" phase. Applying the sol-gel process, it is possible to fabricate ceramic or glass materials in a wide variety of forms: ultra-fine or spherical shaped powders, thin film coatings, ceramic fibers, microporous inorganic membranes, monolithic ceramics and glasses, or extremely porous aerogel materials.

The starting materials used in the preparation of the "sol" are usually inorganic metal salts or metal organic compounds such as metal alkoxides. In a typical sol-gel process, the precursor is subjected to a series of hydrolysis and polymeration reactions to form a colloidal suspension, or a "sol". Further processing of the "sol" enables one to make ceramic materials in different forms. Thin films can be produced on a piece of substrate by spin-coating or dip-coating. When the "sol" is cast into a mold, a wet "gel" will form. With further drying and heat-treatment, the "gel" is converted into dense ceramic or glass articles. If the liquid in a wet "gel" is removed under a supercritical condition, a highly porous and extremely low density material called "aerogel" is obtained. As the viscosity of a "sol" is adjusted into a proper viscosity range, ceramic fibers can be drawn from the "sol". Ultra-fine and uniform ceramic powders are formed by precipitation, spray pyrolysis, or emulsion techniques.

1.2 PROBLEM STATEMENT

The synthesis of nanoparticles with controlled size and composition is of technological interest. In particular, there has been a lot of highlighting on the production of nanoparticulated CdO for a wide range of applications. The photocatalytic activity of CdO powder strongly depends on its microstructural and physical properties such as surface area, crystallinity, phase composition etc. Synthetic routes for CdO nanoparticles are usually based on a sol–gel precipitation from alkoxide precursors, producing an amorphous powder that upon calcination leads to CdO nanoparticles. Therefore producing nanoparticles of CdO with high surface area should be done in order to optimize the photocatalytic activity of CdO. In order to give the required result the control of the product morphology need to be done.

1.3 OBJECTIVE

1. To synthesis Cadmium Oxide nanoparticles by using sol gel method with high surface area
2. To characterize the synthesized Cadmium Oxide by using FT-IR, XRD, SEM and UV-Vis.

1.4 SCOPE OF STUDY

The main scope of study is to synthesize the nanoparticles of CdO with high surface area and to study the morphology of the synthesized CdO after calcinations process. The calcinated CdO will determine the characteristics of the cristallinity of the synthesized CdO. Morphology is a study of shape, size, texture and phase distribution of physical objects. Morphology for the final product of this project will be done by FT-IR (Fourier Transform Spectroscopy), XRD (Powder X-Ray Diffractometry) to study about cristalinity of the synthesized CdO, SEM (Scanning Electron Microscopy) to characterize the phase form after calcination process and UV-Vis to determine the band gap of the CdO.

Calcinations process in one of the vital element in this synthesizing process leading in producing amorphous powder of CdO. Calcination is a thermal treatment process applied to ores and other solid materials in order to bring about a thermal decomposition, phase transition, or removal of a volatile fraction. The calcination process normally takes place at temperatures below the melting point of the product materials. Calcination is to be distinguished from roasting, in which more complex gas-solid reactions take place between the furnace atmosphere and the solids, as calcination takes place in the absence of air. This process most likely to applied in making catalyst and in this project this calcination of heat treatment is mean to effect phase transformations, as in conversion of anatase.

CHAPTER 2

LITERATURE REVIEW

As an important semiconductor substance with the band gap 2.5 eV. Among II–VI compounds, CdO thin films have vast applications in many optoelectronic devices, phototransistors and diodes, transparent electrodes, sensors, etc. These applications are based on its specific optical and electrical properties. It is found that these films show a high transparency in the visible region of solar spectrum, as well as low ohmic resistance. Cadmium hydroxide can be used as a precursor of CdO film. The ability to synthesize CdO nanocrystals with controlled shape, composition, and structure would enable a variety of size-dependent physical properties to be explored, including structural, electronic, and magnetic phase transitions as a function of size, composition, and shape. To improve chemical and physical properties of CdO thin films, researchers are trying to modify the synthesis procedure. (Mane et al, 2005).

Mane et al, 2005, discussed the potential of CdO to be use in Dye-Sensitized solar cell. This study shows that Indium Tin Oxide plate used to dip $Cd(OH)_2$ for several cycle and after being annealed at 250°C for 24hour CdO film formed on that plate. Then surface morphology was studied by SEM and XRD.

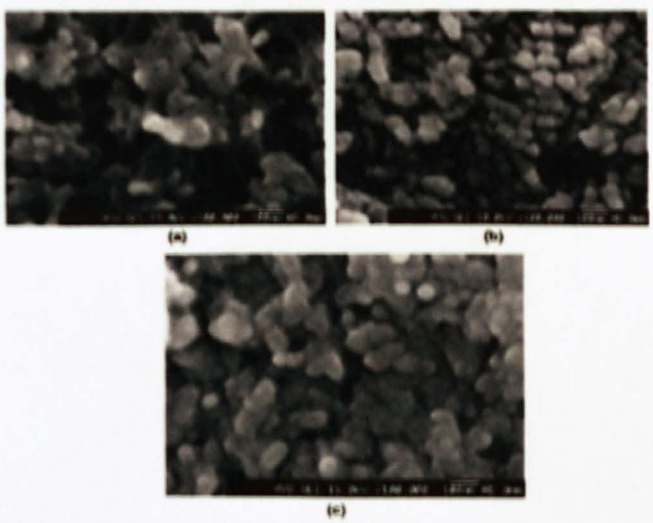

Fig. 1. SEM images of as-deposited $Cd(OH)_2$ (a), ultrasonically cleaned Cd $(OH)_2$ (b), and CdO obtained after calcination at 250 °C for 24 h in air (c). *Mane et al, 2005.*

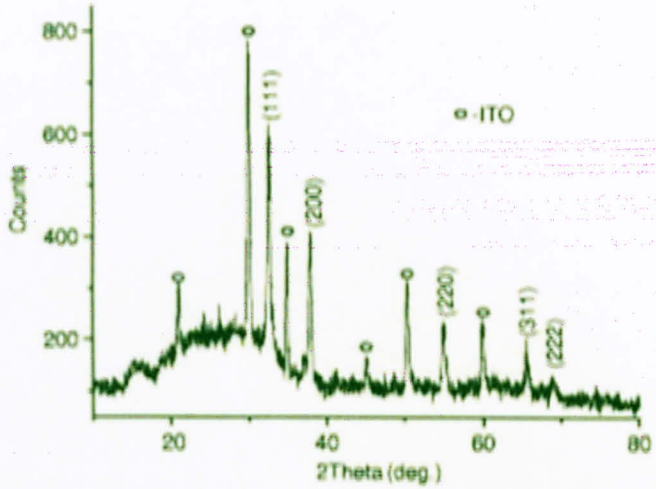

Fig. 2. A typical XRD spectrum obtained for CdO films annealed at 250 °C for 24 h in air. *Mane et al, 2005.*

Mane et al, 2005 conclude in the studies that as revealed by SEM photo-images, as-deposited $Cd(OH)_2$ films possess fiber like surface morphology. During ultrasonic treatment, surface change from fiber to spherical grains was noted due to removal of loosely bounded hydroxyl species. 250 °C for 24 h annealing causes phase change from $Cd(OH)_2$ to CdO as evidenced by XRD. The CdO film shows considerable increase in conversion efficiency from 0.24% to 2.95% due to N3 dye adsorption. However, need of sustained efforts required to improve fill factor.

As reported by Lennstrom et al, 2003 in their studies for synthesizing of cadmium tungstate film via sol-gel method shows that this method successfully produces the single-phase crystalline $CdWO_4$ upon sintering, which is supported by the XRD results. This study also discuss about the precursor being used that might be affected of the formation of the sol. In this study, comparison between tungsten chloride WCl_6 and cadmium acetate of both was being dissolved in ethanol. As reported cadmium acetate is the best precursor upon gelation process to produce $CdWO_4$. This is due to hydrolysis and condensation reactions with the associated water upon dissolution in ethanol. The long gelation time for cadmium alkoxide solution suggested that the hydrolysis and condensation reactions were slow. However, upon introduction of cadmium acetate into the tungsten precursor solution, subsequent hydrolysis and

condensation reactions proceeded very rapidly. The gelation of resulting sols was strongly dependent on the precursor concentration and the solvent type.

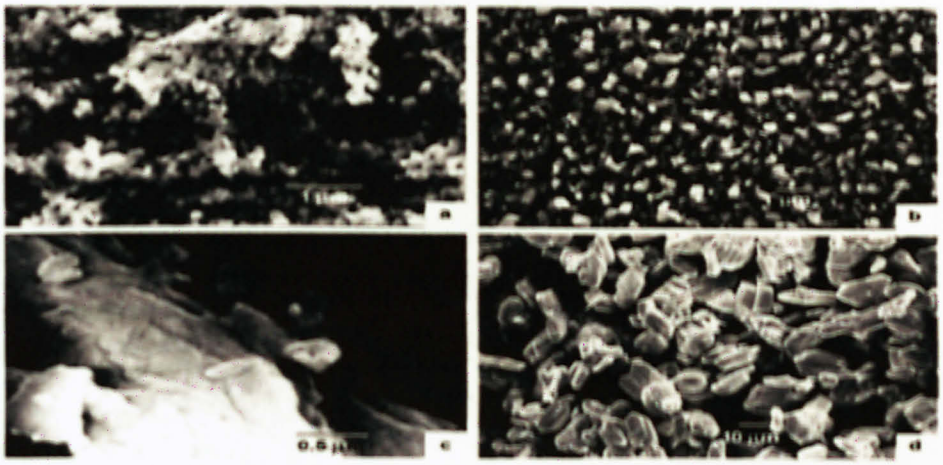

Fig. 3. (a) Thin film of cadmium tungstate gel as deposited on borosilicate glass. The open pore structure likely results from the short gelation time. (b) Thin film of cadmium tungstate deposited on borosilicate glass and sintered at 500 °C for 4 h. The resulting film consists of individual crystals of approximately 1 μm in diameter. (c) Bulk powder of dried cadmium tungstate gel. Agglomerates are thought to have formed, as indicated by fine lines bordering the grains. (d) Bulk powder of cadmium tungstate after sintering at 600 °C for 4 h. The micrograph indicates crystallization of large grains of the order of 10 μm in diameter. *Lennstrom et al, 2003.*

Fig. 4. Film deposited on borosilicate glass, sintered at 500 °C for 4 h. The film was derived from a sol–gel with butanol as a solvent instead of ethanol. The resulting

morphology implies that the solvent has the desired effect of increasing the film density. *Lennstrom et al, 2003.*

Sonochemical and hydrothermal routes have been used in different conditions for preparation of $CdCO_3$ and $Cd(OH)_2$ nanoparticles at air and inert atmospheres, respectively. The CdO nanoparticles were obtained by heating of $CdCO_3$ and $Cd(OH)_2$ nanoparticles at 400 °C. Powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) microscopy have been used to characterize the nanoparticles. The XRD results of intermediate products showed that the origin of $CdCO_3$ is CO_2 from air atmosphere (Askarinejad and Morsali, 2009).

Then, Askarinejad and Morsali, 2009, reported that the synthesis of $CdCO_3$ and CdO nanoparticles from reaction of $Cd(CH_3COO)_2$ and tetramethylammonium hydroxide (TMAH) or NaOH by a sonochemical method under different conditions. They have been using sonochemical and hydrothermal routes to investigate the mechanism of $CdCO_3$ preparation. Table 1 shows the reactions and their conditions which were performed as well as the product before calcination.

Table 1: Reactions and their conditions which were performed as well as the product before calcinations. *Askarinejad and Morsali, 2009*

Reaction number	**Initial materials**	**Atmosphere**	**Solvent**	**Product before calcination**	**Method**
1	50 ml $Cd(CH_3COO)_2$ (0.1 M) + 100 ml TMAH (0.1 M)	Air	EtOH	$CdCO_3$	Sonochemical
2	50 ml $Cd(CH_3COO)_2$ (0.1 M) + 100 ml TMAH	Argon	EtOH	$Cd(OH)_2$	Sonochemical

Reaction number	Initial materials	Atmosphere	Solvent	Product before calcination	Method
	(0.1 M)				
3	50 ml $Cd(CH_3COO)_2$ (0.1 M) + 100 ml NaOH (0.1 M)	Argon	EtOH	$Cd(OH)_2$	Sonochemical
4	50 ml $Cd(NO_3)_2$ (0.1 M) + 100 ml NaOH (0.1 M)	Air	EtOH	$Cd(OH)_2 + CdCO_3$	Sonochemical
5	50 ml $Cd(CH_3COO)_2$ (0.1 M) + 100 ml NaOH (0.1 M)	Argon	EtOH + H_2O	$Cd(OH)_2 + Cd_3(OH)_5(NO_3)$	Hydrothermal
6	50 ml $Cd(NO_3)_2$ (0.1 M) + 100 ml NaOH (0.1 M)	CO_2	EtOH	$CdCO_3$	Sonochemical
7	50 ml $Cd(CH_3COO)_2$ or $Cd(NO_3)_2$ (0.1 M) + 100 ml NaOH (0.1 M)	Air	EtOH + H_2O	$CdCO_3$	Simple titration

Table 1 disscussed about the obtained product before calcination process. As perdiscussed reaction 1 produce Cadmium Carbonate as observed by XRD, reaction 2 produced cadmium hydroxide with a hexagonal crystal structure and lattice parameters of $a = 3.4947$, $c = 4.7106$, $z = 1$ and space group = $P3m1$ (JCPDS card number 31-

0228). In the reaction no. 3, NaOH has been used instead of TMAH and the result is the same as the reaction no. 2. In the reaction no. 4 $Cd(NO_3)_2$ was used as precursor and the reaction was performed in air atmosphere and the XRD pattern of the obtained product shows a mixture of $Cd(OH)_2$ and $CdCO_3$. Sample no. 5 is obtained by a hydrothermal method and characterized as a mixture of $Cd(OH)_2$ and $Cd_3(OH)_5(NO_3)$. In the reaction no. 6, CO_2 is purged to the reaction of $Cd(NO_3)_2$ and NaOH in an ultrasonic bath, the product obtained by this procedure is $CdCO_3$.

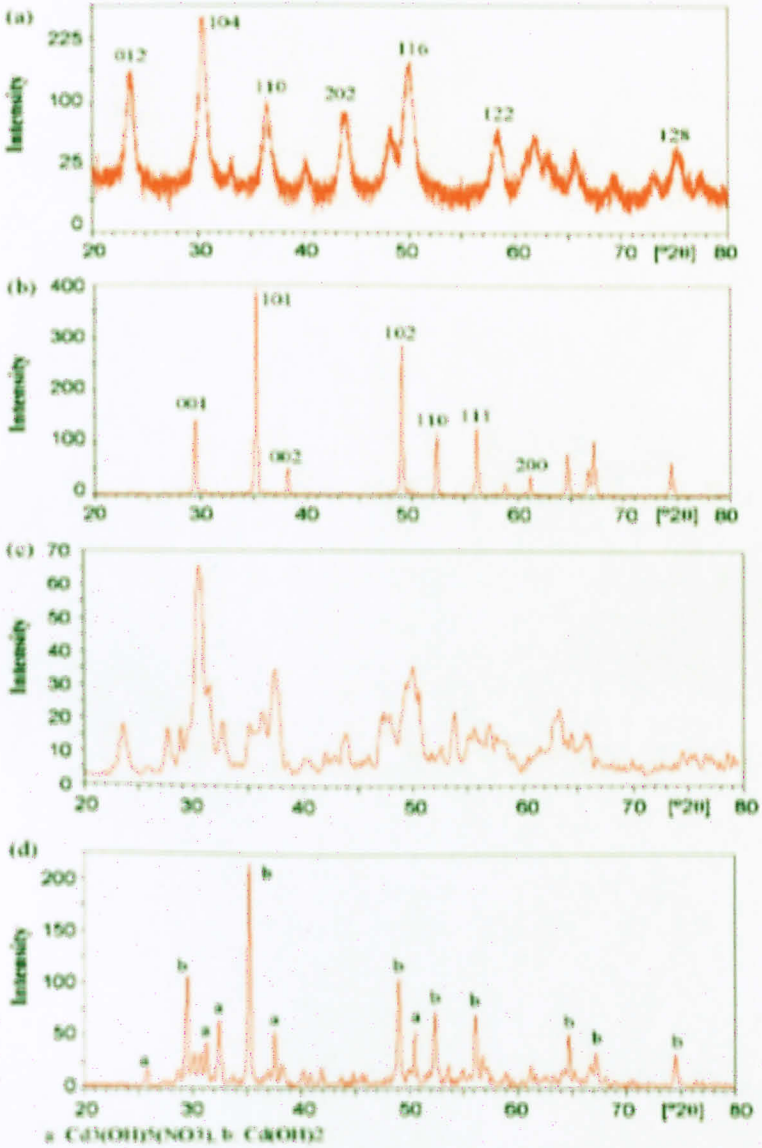

Fig. 5. The XRD pattern of (a) $CdCO_3$ nanoparticles of sample no. 1, (b) $Cd(OH)_2$ nanoparticles of sample no. 2, (c) a mix of $CdCO_3$ and $Cd(OH)_2$ nanoparticles of sample

no. 4 and (d) a mix of $Cd(OH)_2$ and $Cd_3(OH)_5(NO_3)$ nanoparticles of sample no. 5. *Askarinejad and Morsali, 2009.*

In all the reactions, the CdO nanoparticles are the result of calcinations at 400 °C. Figure 6a shows the SEM image of the intermediate product and figure 6b shows the SEM image of CdO nanoparticles of the reaction no. 4.

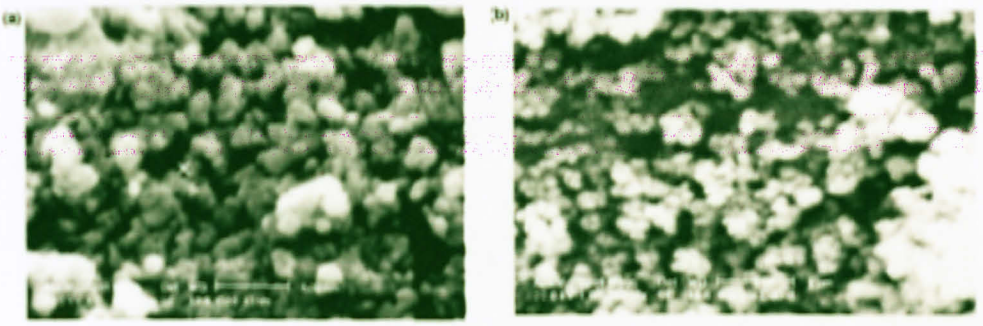

Fig. 6. The SEM image of (a) the intermediate product ($Cd(OH)_2$ + $CdCO_3$ nanoparticles) and (b) CdO nanoparticles obtained by calcination of the intermediate product (reaction no. 4). *Askarinejad and Morsali, 2009*

The result obtaining from the performing reactions has been summarized in figure 7.

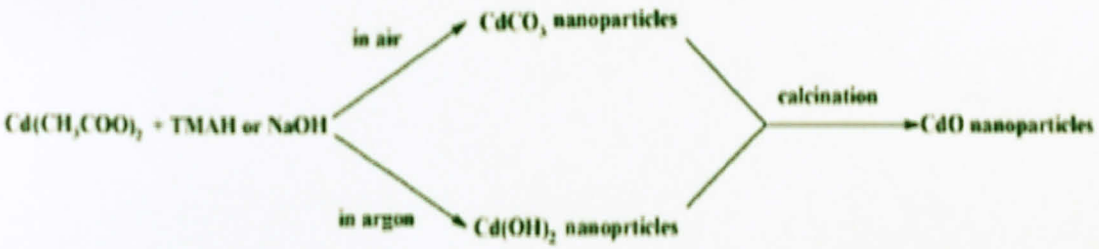

Fig.7. Schematic diagram of the reaction, intermediate product and final products upon calcinations. *Askarinejad and Morsali, 2009.*

As it can be seen in figure 7, the intermediate product of the reaction of cadmium acetate and TMAH or NaOH is cadmium carbonate nanoparticles in air

atmosphere and in the existence of carbon dioxide, and cadmium hydroxide nanoparticles in inert atmosphere and the final product upon calcinations is CdO nanoparticles.

From this literature review of Askarinejad and Morsali, 2009, the most concern matter is about the finding of the best calcinations temperature for the desired product. It shows that upon the calcinations whatever the intermediate product is the final product will be CdO which is the author most concern about but still depends on the precursor being used. Eventually proved that simple sonochemical route and a hydrothermal route by modifying the different parameters have been used to successful ‹synthesis› of CdO nanoparticles. Different intermediates have been obtained by using different precursors, different methods and different atmospheres. The obtained products have been analyzed by means of SEM and XRD. The XRD results showed that $CdCO_3$ and $Cd(OH)_2$ nanoparticles were obtained in air and inert atmospheres, respectively.

Maity and Chattopadhyay, 2005, was discussed about aluminum-doped cadmium oxide (CdO:Al) thin films are deposited on glass substrates by the sol–gel dip-coating method, taking cadmium acetate dihydrate as the precursor material. Aluminum nitrate has been taken as a source of Al-dopant. XRD pattern reveals the good crystallinity of CdO thin films. From this literature review the author concern about the method being used in producing the CdO nanoparticles which is sol-gel process. SEM micrograph showed the presence of faceted crystallites.

The typical XRD pattern of aluminum-doped cadmium oxide thin film for 10% of Al-doping is shown in figure 8. The 3 main peaks for (1 1 1), (2 0 0) and (2 2 0) reflections originated at the 2θ values 33.09°, 38.54° and 55.28°, with corresponding 'd' values 2.704, 2.333 and 1.660 Å, which indicated the cubic phase formation.

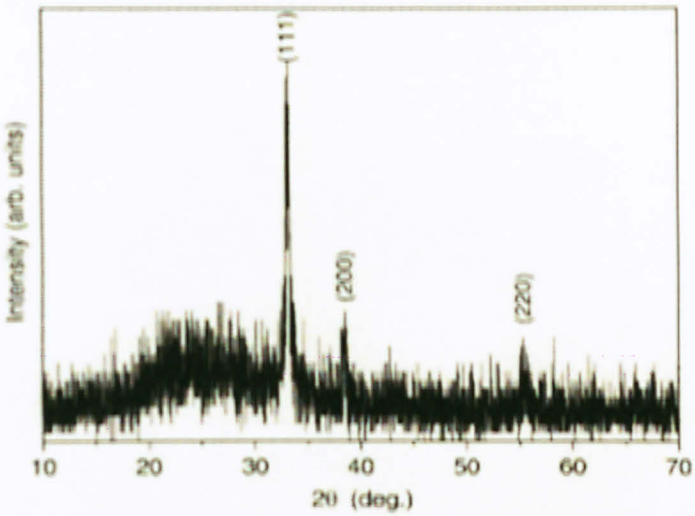

Fig. 8. Typical XRD spectrum of CdO:Al thin film. *Maity and Chattopadhyay, 2005*

Figure 9 show the SEM of an Al-doped CdO thin film deposited on a glass substrate. The micrograph shows the existence of well-crystallized grains, having a faceted structure, with an average grain size of ~0.5 μm.

Fig. 9. (a) and (b) SEM micrograph of CdO:Al thin films for different magnifications. *Maity and Chattopadhyay, 2005.*

From the studied by Maity and Chattopadhyya aluminum-doped cadmium oxide thin films are deposited on glass substrates by sol–gel dip-coating method successfully. The XRD pattern reveals the good crystallinity of CdO thin films, and also a proper cubic phase formation. SEM micrograph showed the well-faceted structure. Optical study shows the 40–85% transparency in the visible region, with a bandgap value lying in the range 2.76–2.52 eV, depending upon the Al content in the films.

A chemical synthesis process for the fabrication of CdO nanowires is described. In the present work, transparent and conductive CdO films were synthesized on the glass substrate using chemical bath deposition (CBD) at room temperature. These films were annealed in air at 623 K and characterized for the structural, morphological, optical and electrical properties were studied by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), optical and electrical resistivity. The XRD analysis showed that the as-deposited amorphous can be converted in to polycrystalline after annealing. Annealed CdO nanowires are 60–65 nm in diameter and length ranges typically from 2.5 to 3 μm. The optical properties revealed the presence of direct and indirect band gaps with energies 2.42 and 2.04 eV, respectively. Electrical resistivity measurement showed semiconducting behavior and thermoemf measurement showed n-type electrical conductivity Dhawale et al, 2007. From this study shows the process was successfully done in the room temperature. This can narrow down the study of reactions atmosphere that being done by Askarinejad and Morsali, 2009.

Dhawale et al, 2007, reported to synthesized CdO by Chemical Bath Deposition(CBD) at room temperature. Form the study it shows that CBD is based on the formation of solid phase from a solution, which involves two steps as nucleation and particle growth. In the nucleation, the clusters of molecules formed undergo rapid decomposition and particle combine to grow up to a certain thickness of the film by heterogeneous reactions at the substrate surface. For the deposition of CdO film, $CdCl_2$ is used as source of cadmium. When the ammonia is added to it, white precipitate occurred, which got dissolved by additional ammonia.

Figure 10 (a and b) shows X-ray diffractograms of as-deposited and annealed at 623 K CdO thin films deposited on glass substrate, respectively. Inset of figure shows photographs (a) as-deposited and (b) annealed CdO films. The photo-images shows whitish color of as-deposited film which turned brown after annealing at 623 K. The as-deposited CdO thin films were amorphous while annealing these films at temperature 623 K crystallizes the film. The annealed film showed those XRD reflections which correspond very well with NaCl structure of CdO. It also indicates the presence of (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (4 2 0) planes for cubic CdO. The lattice parameter '*a*' is calculated for cubic structure of CdO film. The calculation lead to '*a*' = 4.68 Å which is in good agreement with standard '*a*' value.

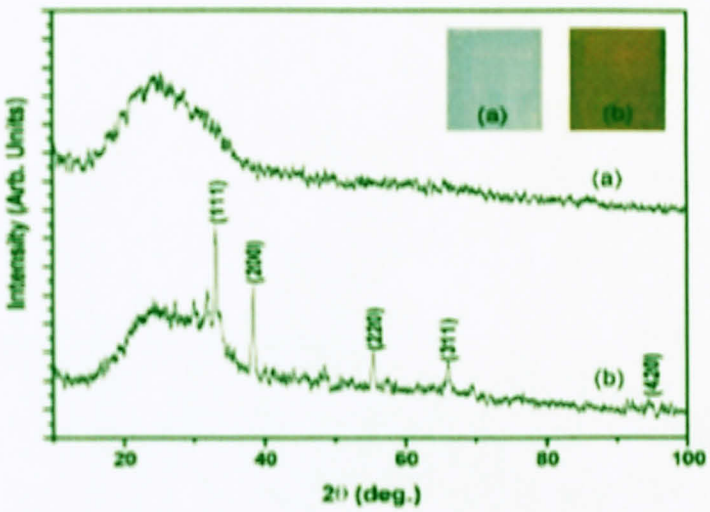

Fig. 10. The X-ray diffractograms of (a) as-deposited and (b) annealed at 623 K CdO thin films (inset shows photographs (a) as-deposited and (b) annealed CdO films). *Dhawale et al, 2007.*

While for the surface morphology study, Dhawale et al, 2007, reported that the nanowires formed primarily as metallic cadmium and their surfaces subsequently became oxidized when the sample was exposed to air, since cadmium can be readily oxidized under ambient conditions.Figure 11 (a and b) shows the SEM images of annealed CdO films at two different magnifications. The low magnification (Fig. 11a) image confirms the interconnected CdO nanowires. The wires are relatively smooth

with randomly distributed on the glass substrate and their diameters are uniform. For detail investigation of these nanowires, high magnified image (Fig. 11b) is recorded which gives a description that these nanowires are with 60–65 nm in diameter and length typically ranges from 2.5 to 3 μm. As an application to dye-sensitized solar cells (DSSCs) as well as gas sensors, the CdO electrode composed of several nanowires of micrometers in length created a window of curiosity in our mind.

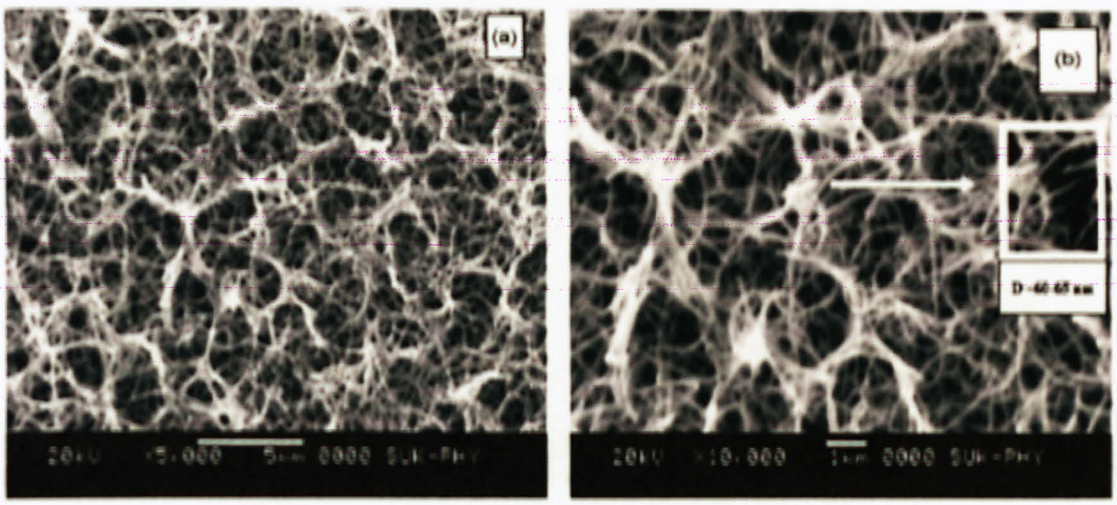

Fig. 11. The SEMs of annealed CdO thin film at the magnifications of (a) 5000× and (b) 10,000× (inset shows a typical nanowire of 60–65 nm in diameter). *Dhawale et al, 2007.*

Dhawale et al, 2007, concluded that an aqueous solution system for growing CdO nanowires network was investigated. The present method is simple, economic and easily reproducible for cadmium oxide nanowires. Through XRD examination, it has been concluded that amorphous CdO thin films could be converted into polycrystalline after annealed at 623 K. The optical transmittance measurement showed that the CdO films has flat surface, a high average transmittance over 80% in the visible region with presence of direct and in-direct band gaps having energies 2.42 and 2.04 eV,

respectively. From the electrical study, it was found that the films of CdO were semiconducting with n-type electrical conductivity.

Some study of Cadmium hydroxide ($Cd(OH)_2$) and cadmium oxide (CdO) nano and micro crystals were synthesized in ethanol–water medium using cadmium foil both as a source and substrate under solvothermal condition. Different concentrations of ammonium hydroxide, hydrazine hydrate, sodium hydroxide and potassium hydroxide were added to study the structural and morphological variations in the products. Synthesis was carried out at different temperatures to study the growth stages of the nano/microstructures. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The as-prepared $Cd(OH)_2$ products were transformed to CdO by thermal treatment in air. The possible growth mechanism for the formation of different morphologies at different basic medium has been proposed. The optical absorption measurement was carried out to determine the values of the band gap of CdO, Ghoshal et al, 2009.

Crystal structure and phase of the samples prepared in ethanol (E)–water (W) medium (E:W = 5:3) with different concentrations of the bases at temperature 200 °C was determined from the XRD pattern (Figure 12). By keeping the temperature constant and varying the base concentration this can determine the effect the base concentration upon the desired product.

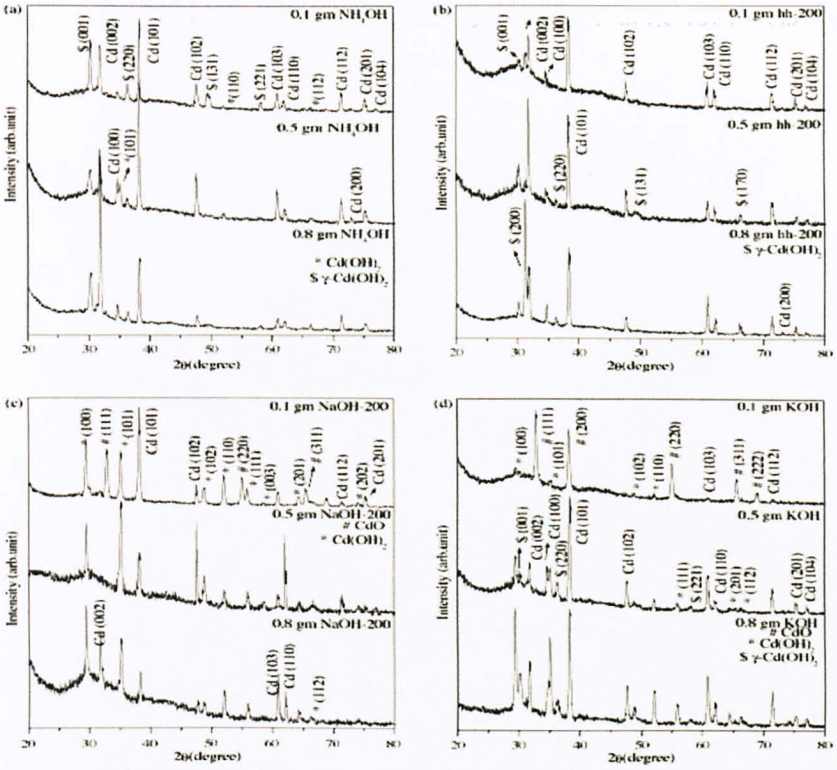

Fig. 12. XRD pattern of the samples prepared with 5:3 volume ratio of ethanol to water at a temperature 200 °C using different amounts of (a) ammonium hydroxide (b) hydrazine hydrate (c) sodium hydroxide and (d) potassium hydroxide. *Ghoshal et al, 2009.*

In order to study the effect of temperature on the phase of the products, the synthesis was performed at different temperatures keeping the base concentration constant. Figure 13 shows the XRD pattern of the products prepared with 0.5 gm NH_4OH at different synthesis temperatures. For the samples synthesized at lower temperature (160 °C), both cubic structured cadmium oxide and hydroxide phases appeared. But with the increase in the synthesis temperature, hexagonal and monoclinic phases of cadmium hydroxide were formed. The XRD patterns indicated the formation of well crystallined products. To test the feasibility of the products, the $Cd(OH)_2$ sample prepared with 0.5 gm NH_4OH at 200 °C was annealed in air at 300 °C for 2 h and 200 °C for 4 h and corresponding XRD pattern revealed that the hydroxide was completely transformed to CdO phase.

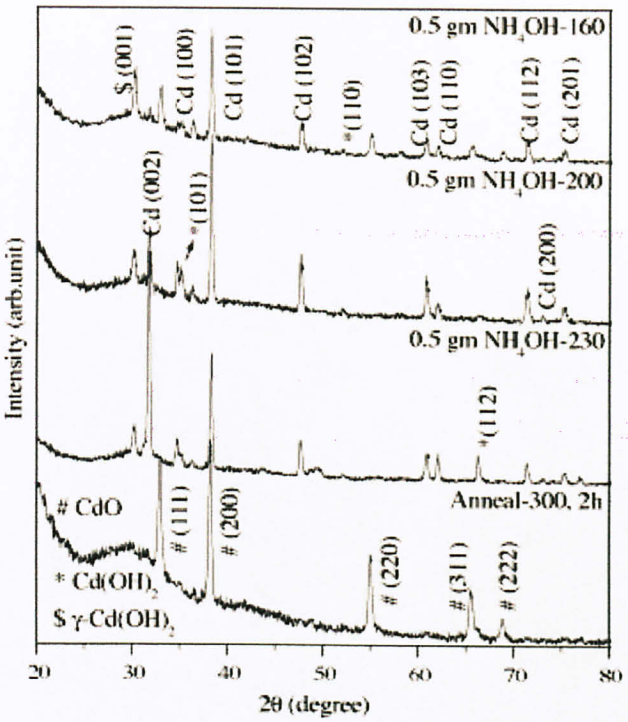

Fig. 13. XRD pattern of the samples prepared with ammonium hydroxide at different temperatures (160 °C, 200 °C, 230 °C) and the sample annealed at 300 °C for 2 h. *Ghoshal et al, 2009.*

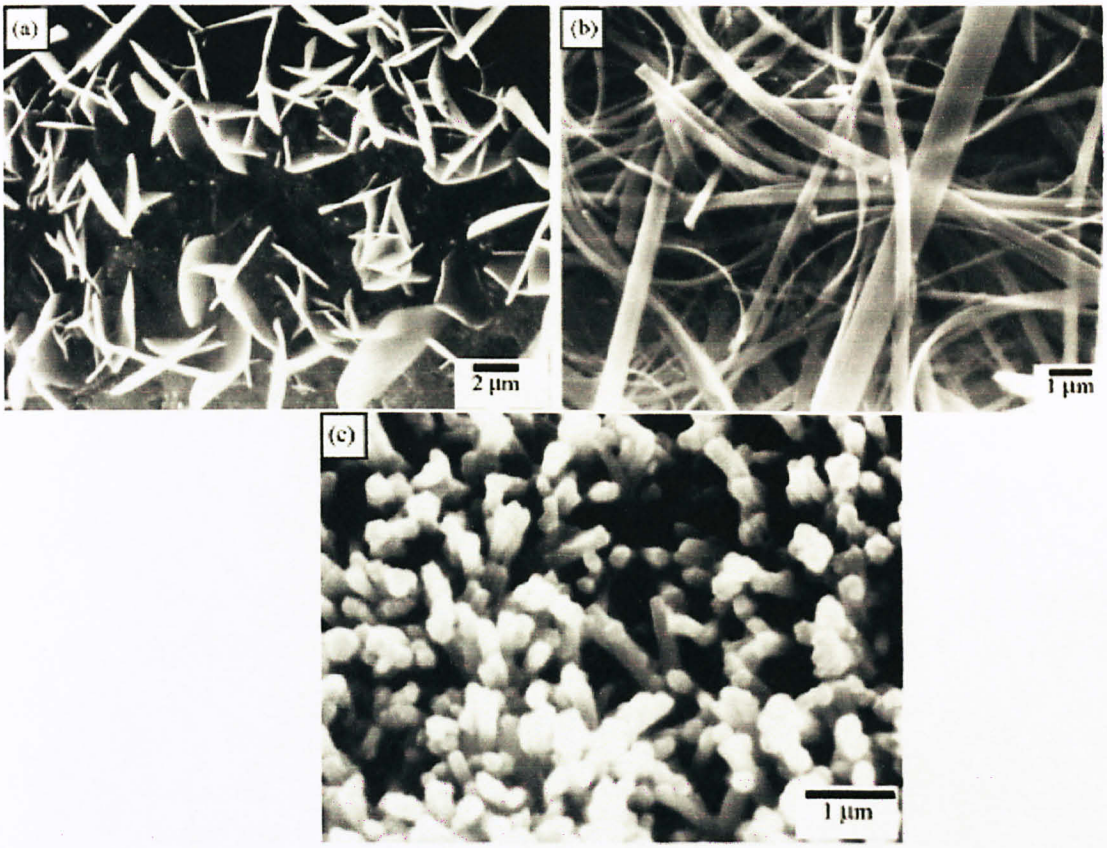

Fig. 13. SEM images of the product prepared at temperature 200 °C using (a) 0.1 gm (b) 0.5 gm and (c) 0.8 gm ammonium hydroxide. *Ghoshal et al, 2009.*

For the microstructural analysis reported by Ghoshal et al, 2009, the as-synthesized samples were directly transferred to the SEM chamber without disturbing the original nature of the products. Fig. 13a shows the morphology of sample prepared with 0.1 gm NH_4OH synthesized at temperature 200 °C. It consists of large number of flakes randomly distributed over the base foil. Most of them were interconnected with each other making different angles between them. Fig. 3b reveals that the sample prepared with 0.5 gm NH_4OH consists of a large quantity of ribbon-like structure with typical lengths in the range of several micrometers. The image shows either single ribbon or a bundle of single nanoribbons. Fig. 13c The rods were uniformly distributed throughout the foil and most of the rods were oriented in the upward direction. The

cross-section of all the rods was hexagonal and uniform throughout their entire length. The nanorods were found to have diameter in the range from 200 nm to 350 nm. Different morphologies of $Cd(OH)_2$ were formed for different concentrations of NH_4OH.

While in order to study the effect of temperature, Ghoshal et al, 2009, had conducted the experiment at two different temperatures 160 °C and 230 °C for two different concentrations of NH_4OH. The sample prepared with 0.5 gm NH_4OH at temperature 160 °C consists of large number density of well-edged polyhedrons throughout the foil (Fig. 14d). Same morphological feature was obtained for higher amount of NH_4OH at temperature 160 °C. FESEM image shown in fig. 14e exhibits large quantity of nanowires obtained at higher synthesis temperature 230 °C. The nanowires have diameters in the range 40–80 nm and the bending of the nanowires was not sharp enough. Small diameter nanowires were also seen from this figure lying below these nanowires. Some of the nanowires were found to have non-uniform diameters through their entire lengths. The surfaces of the nanowires were not smooth. The morphology remained almost same at higher synthesis temperature 230 °C for highest concentration of NH_4OH. Fig. 14f shows large number of nanowires of CdO when the sample prepared with 0.5 gm NH_4OH at 200 °C was annealed at 300 °C for 2 h in air. Nanowires consisted of ensembles of faceted grains stacked along the length of the wire giving pearl necklace type morphology. The nanowires were of few micrometers in length.

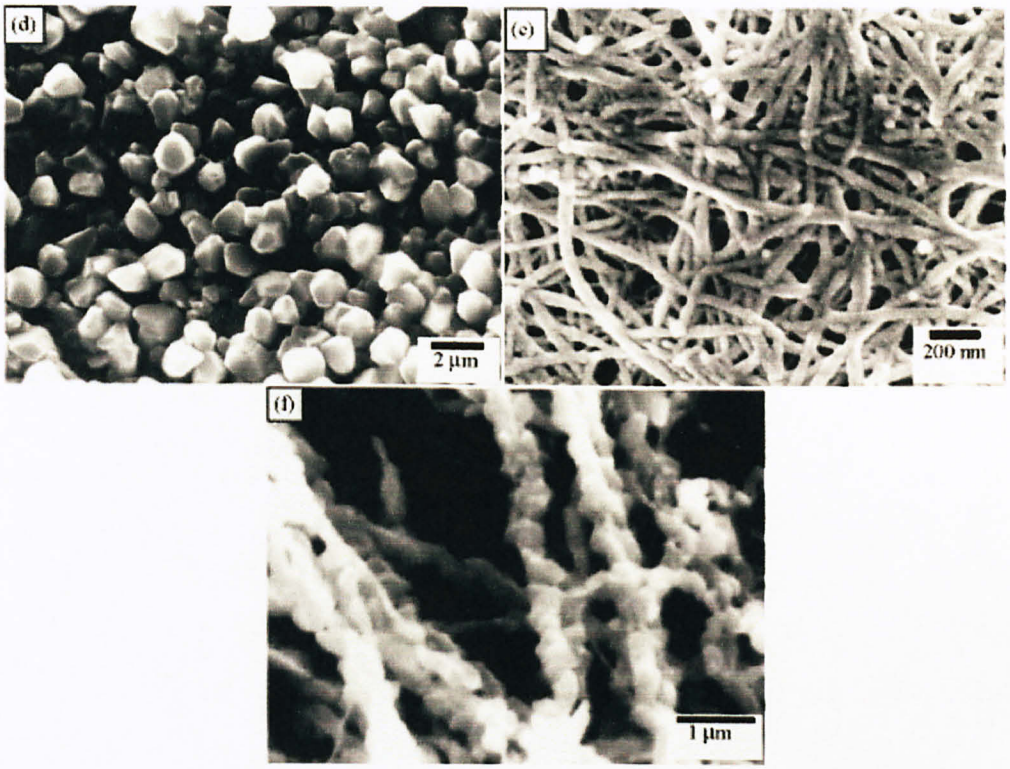

Fig. 14. SEM image of the sample prepared with ammonium hydroxide at temperatures (d) 160 °C and (e) 230 °C. (f) Sample annealed at 300 °C for 2 h. *Ghoshal et al, 2009.*

Another matter concerned from this study of Ghoshal et al, 2009 is about the effect of morphology from different concentrations of NaOH. Using 0.1 gm NaOH, rod-like morphology was obtained. Rods were randomly and fairly uniformly distributed throughout the foil (fig. 15a). The diameters of the nanorods varied in the range between 130 nm and 300 nm. Some large diameter nanorods were visible from this figure. These large diameter nanorods were actually nanorod bundles formed when two or more small diameter nanorods were joined together through their side facets. The diameters of these nanorods were uniform throughout its entire length. Large number of $Cd(OH)_2$ sheets were formed for the sample prepared with 0.5 gm and 0.8 gm NaOH shown in fig. 15b. Most of the nanosheets were oriented vertically in the upward direction so that their thickness could be easily measured. The thickness of the $Cd(OH)_2$ sheets ranged from 60 nm to 160 nm. Two or more nanosheets were joined with each

other forming an interconnected porous structure. No separate or isolated nanosheets were observed in the overall region of the foil.

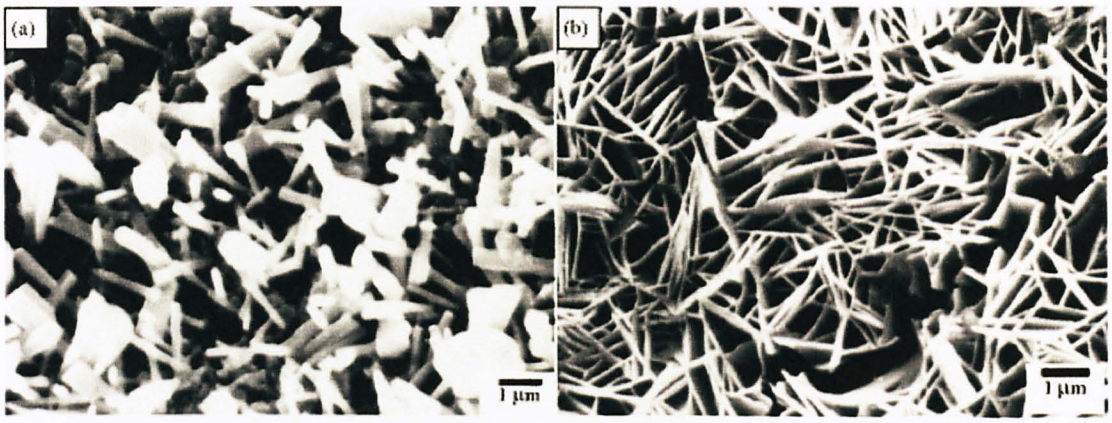

Fig. 15. SEM images of the samples synthesized with (a) 0.1 gm (b) 0.5 gm of NaOH at temperature 200 °C. *Ghoshal et al, 2009.*

Different morphologies of $Cd(OH)_2$ and CdO nano/microstructures such as flakes, ribbons, rods, and wires were successfully synthesized, based on a simple solvothermal process using ethanol–water mixture as a solvent. This is an easily controllable technique for varying the morphologies and phase of the product by just varying the nature and concentrations of bases. The as-prepared $Cd(OH)_2$ nano/microstructures was transformed to CdO by low temperature annealing in ambient atmosphere. The possible growth mechanism for the formation of nano/microcrystallites has been proposed. The absorption measurement for the annealed CdO sample shows slightly higher direct and indirect values of band gaps as 2.52 eV and 1.78 eV respectively. Ghoshal et al, 2009.

From the review the author can conclude that there is several methods in synthesizing of CdO nanoparticles whilst the main focus is in the sol-gel method. As discussed in the preview some parameters need to be considered are Ph value, peptisation temperature, solution concentrations, stirring, heat treatment as well as the shape controller such as amines groups.

CHAPTER 3

METHODOLOGY

3.1 FLOW CHART OF THE EXPERIMENT

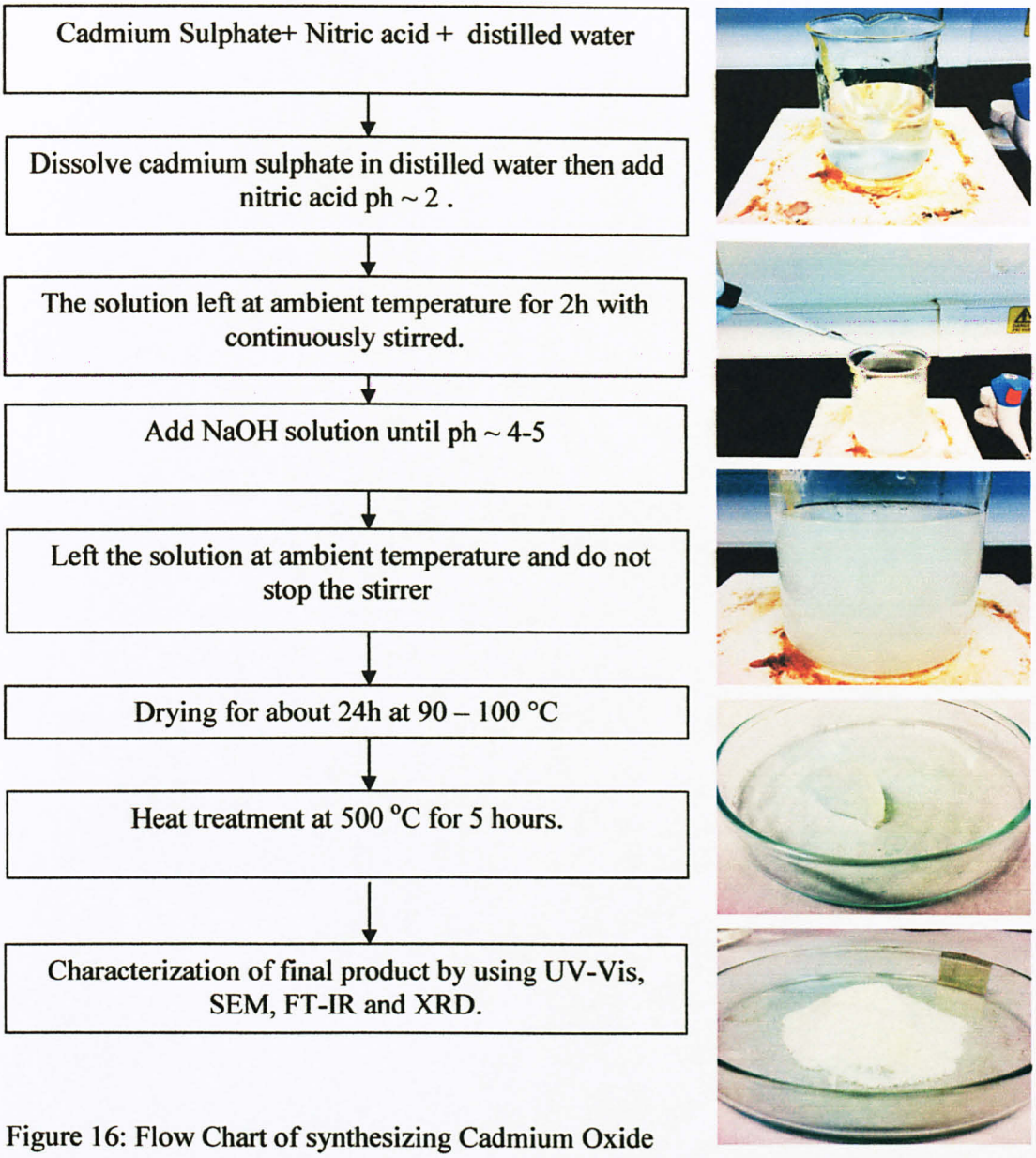

Figure 16: Flow Chart of synthesizing Cadmium Oxide using sol-gel method.

3.2 EXPERIMENTATION AND METHODOLY

A solution of cadmium sulphate with nitric acid, will be prepared. The solution will then be added into 100 ml of distilled water and stirred vigorously using magnetic stirrer until formed gel. It will then be dried by using vacuum drying at 80 °C for 3 hours. Calcination (heat treatment) will be done at 400, 500 and 600°C for overnight. Morphology study of the final product will be done by using FT-IR, XRD, SEM and UV-Vis. Characterization such as surface area of the nanoparticles, crystal phase (anatase or rutile), and phase fraction will be studied.

As discussed before, calcinations process will be done to bring about a thermal decomposition, phase transition, or removal of a volatile fraction. The calcination process normally takes place at temperatures below the melting point of the product materials. Calcination is to be distinguished from roasting, in which more complex gas-solid reactions take place between the furnace atmosphere and the solids, as calcination takes place in the absence of air. This process most likely to applied in making catalyst and in this project this calcination of heat treatment is mean to effect phase transformations, as in conversion of anatase. The calcinations need to be determined before the calcinations process take place. Therefore Thermo Gravimetric Analysis is required in order to determine the optimum calcinations temperature.

3.2.1 Thermogravimetric Analysis (TGA)

Thermal Gravimetric Analysis (TGA) is a simple analytical technique that measures the weight loss (or weight gain) of a material as a function of temperature. As materials are heated, they can lose weight from a simple process such as drying, or from chemical reactions that liberate gasses. Some materials can gain weight by reacting with the atmosphere in the testing environment. Since weight loss and gain are disruptive processes to the sample material or batch, knowledge of the magnitude and temperature range of those reactions are necessary in order to design adequate thermal ramps and holds during those critical reaction periods, .

The analyzer usually consists of a high-precision balance with a pan (generally platinum) loaded with the sample. The pan is placed in a small electrically heated oven with a thermocouple to accurately measure the temperature. The atmosphere may be purged with an inert gas to prevent oxidation or other undesired reactions. A computer is used to control the instrument.

Analysis is carried out by raising the temperature gradually and plotting weight against temperature. The temperature in many testing methods routinely reaches 1000°C or greater, but the oven is so greatly insulated that an operator would not be aware of any change in temperature even if standing directly in front of the device. After the data is obtained, curve smoothing and other operations may be done such as to find the exact points of inflection.

A method known as hi-res TGA is often employed to obtain greater accuracy in areas where the derivative curve peaks. In this method, temperature increase slows as weight loss increases. This is done so that the exact temperature at which a peak occurs can be more accurately identified.

3.2.2 Observation of the Size and Shape of the Particles

The products were washed with distilled water and observed using a JEM-1200EX II transmission electron microscope (**TEM**) with an acceleration voltage of 120 kV and a Hitachi S-4100L scanning electron microscope (**SEM**).

3.2.3 Characterization

For the identification of the products, X-ray diffractometry (**XRD**).

CHAPTER 4

RESULT AND DISCUSSION

4.1 EFFECT OF NaOH in SOL-GEL PROCESS

In this study, the author made comparison regarding the effect of NaOH for this sol-gel process. The time taken for the sample completely formed gel is recorded in order to determine, which route of the sol-gel is the best. However, this comparison only for the time taken to formed gel but then the morphology study is not consider yet for this part of report. Table 2 shows the comparison of time taken to formed gel for each sample.

Table 2: Time taken for various samples towards the effect of NaOH

Sample	Time (hours)
1	2.5
2	4
3	2.5
4	2.5

Below is the summary of the sample for Table 2:

1. Cadmium Sulphate + Water + HNO3 + TEOS + Ethanol + NaOH
2. Cadmium Sulphate + Water + HNO3 + TEOS + Ethanol (no addition of NaOH)
3. Cadmium Sulphate + Ammonium Iron Sulphate + Water + HNO3 + TEOS + Ethanol + NaOH
4. Ammonium Iron Sulphate + Water + HNO3 + TEOS + Ethanol + NaOH

From table 2, it shows that with existence of NaOH in the solution will affect the time taken for the sol-gel process. Sample 2, takes the longest time, 24 hours to form gel without addition of NaOH while for others samples with addition of NaOH the time taken around 2.5 hours to form gel is shorter than sample 2. This to be proved by sample 3 with addition of Ammonium Iron Sulphate the time taken to form gel also 2.5

hours while the reaction of Ammonium Iron Sulphate itself also 2.5 hours to form gel with addition of NaOH.

4.2 CALCINATIONS PROCESS

In this report the author had calcine 3 samples at temperature of 400°C and 500°C. After the calcinations process the author make the comparison about the physical change of the sample. The summary for the 3 samples as shows below:

1. Cadmium Sulphate + Water + HNO3 + TEOS + Ethanol + NaOH
2. Cadmium Sulphate + Water + HNO3 + TEOS + Ethanol (no addition of NaOH)
3. Cadmium Sulphate + Barium Nitrate + Water +HNO3 + TEOS + Ethanol + NaOH

Figure 17 shows the physical change of sample 1. From the figure the author observe that the grain size of the sample become more amorphous as the calcinations temperature increase.

Fig 17: Sample 1. (a) sample dry at 90°C after sol-gel process, (b) after calcine at 400°C, (c) after calcine at 500°C

Figure 18 shows the physical change of sample 2. From the figure the author observed that the grain size of the sample become clearer and the distribution of grain size is in position as the calcinations temperature increase. Whilst, the powder become more shining and crystal already form at this state. This differs from sample 1 may to the
effect of NaOH addition, since for this sample no NaOH added.

Fig 18: Sample 2. (a) sample dry at 90°C after sol-gel process, (b) after calcine at 400°C, (c) after calcine at 500°C.

Figure 19 shows the physical change of sample 3. From the figure the author observed that the grain size of the sample become clearer and the distribution of grain size is in position and the powder finer as the calcinations temperature increase. Another physical change observed is the colour of the powder become brownish from 400°C to 500°C. This differs from other sample because might due to addition of Barium Nitrate in the solution.

Fig 19: Sample 3. (a) sample dry at 90°C after sol-gel process, (b) after calcine at 400°C, (c) after calcine at 500°C.

From the physical change of the sample, the author can conclude that the calcinations temperature will affect the morphology of the final product after characterization.

4.3 Usage of TetraEthyl ortosilicate (TEOS)

The usage of TEOS is a base or platform for the Cadmium or Cadmium.Barium to form gel. The author also tests another sample without addition of TEOS, the solution taking longer time to form gel. Addition of TEOS in the process becomes a vital element in order to ensure gel is form and the time taken becomes faster. Table 3 shows the different time taken for the process to form gel with and without addition of TEOS.

Table 3: Time taken for sample to form gel due to with/without addition if TEOS

Sample	Time (hours)
1	2.5
2	96

1. Sample 1: Cadmium Sulphate + Barium Nitrate + Water +HNO3 + TEOS + Ethanol + NaOH
2. Sample 2: Cadmium Sulphate + Barium Nitrate + Water +HNO3 + Ethanol + NaOH (No addition of TEOS)

From table 3 shows that sample 1 only take about 2.5 hours to from gel while sample 2 takes about 4days to from gel. For the improvement of the process the author uses TEOS as the base or platform to form gel.

4.4 Scanning Electron Microscopy (SEM)

Below is the sample that being characterized using SEM :

1. Cadmium Sulphate + Water + HNO3 + TEOS + Ethanol + NaOH
2. Cadmium Sulphate + Water + HNO3 + TEOS + Ethanol (no addition of NaOH)
3. Cadmium Sulphate + Barium Nitrate + Water +HNO3 + TEOS + Ethanol + NaOH

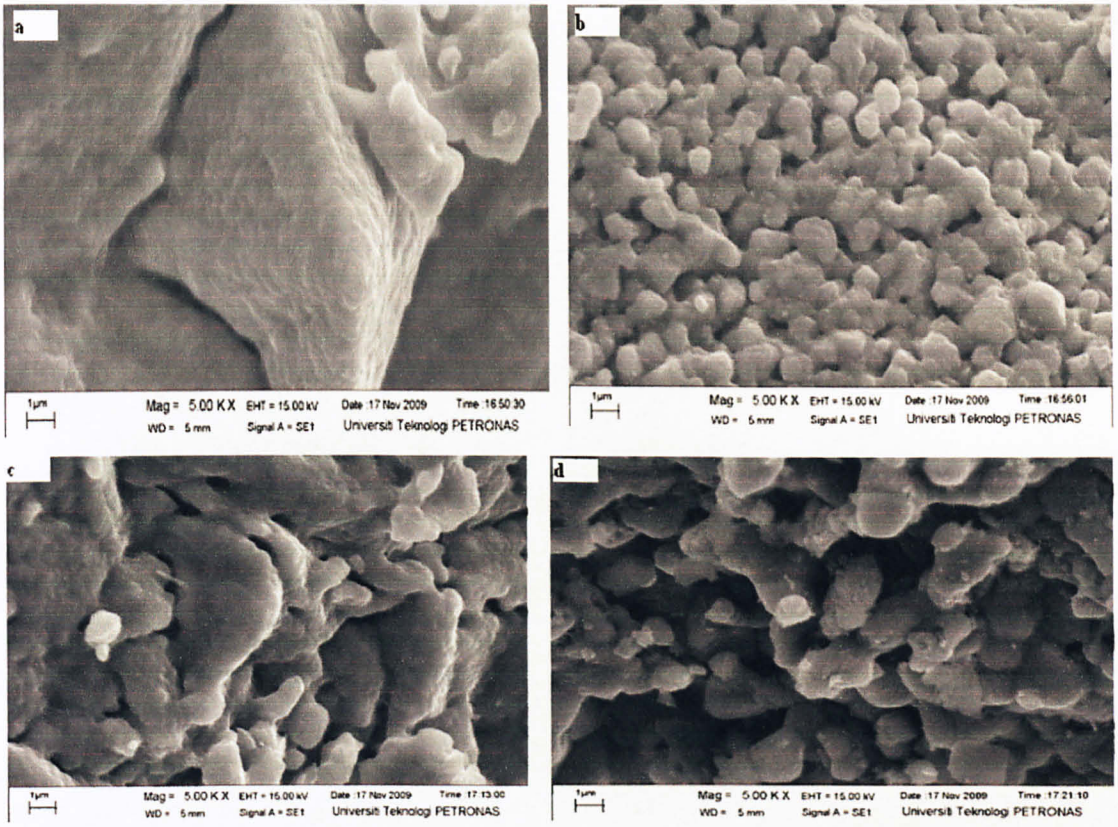

Fig 20: a)Sample 1 calcined at 400°C b) sample 1 calcined at 500°C, c)Sample 2 calcined at 400°C d) sample 2 calcined at 500°C

Figure 20 shows that as sample being calcine at higher temperature the particles are scattered widely. This can lead to large surface area while the metal surface area becomes smaller. This is due to at 400°C the hydrogen compound from TEOS is not fully decompose yet then the gap between the particles is smaller than at 500°C the hydrogen compound is more decompose and lead to the large gap that forming pore between the particles. Therefore as the calcinations temperature increase the surface area will increase but the metal/particles surface area become smaller.

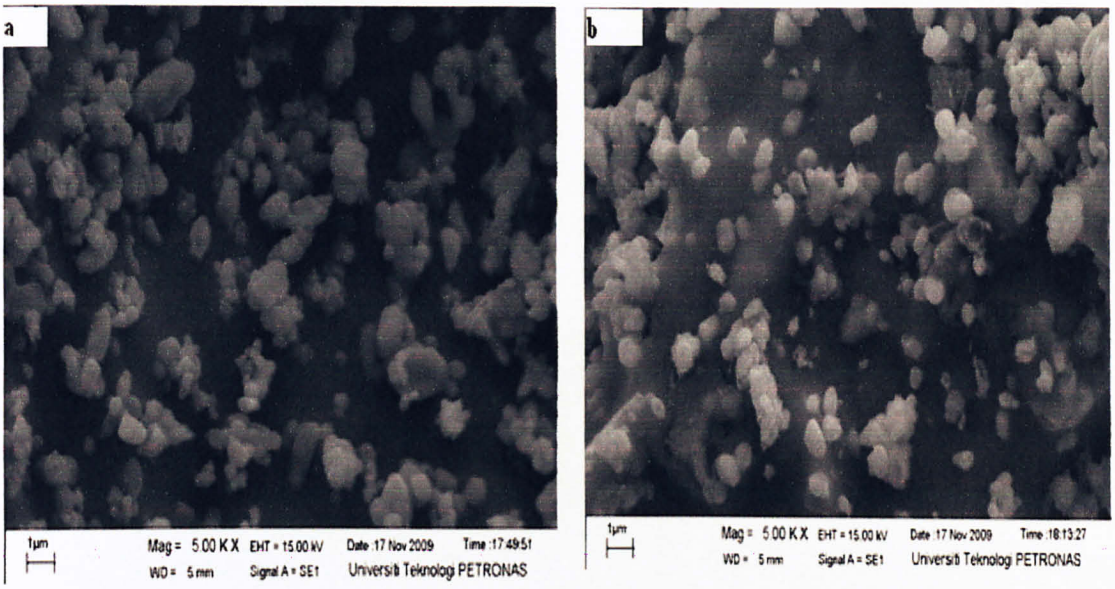

Fig 21: a)Sample 3 calcined at 400°C b) sample 3 calcined at 500°C

Figure 21 indicate that the SEM result of sample 3. For this sample the [articles start to scattered widely as from 400°C. While at 500°C there are some formations of rod. For further clarification the magnification of SEM being increase to get clearer about the formations of rod.

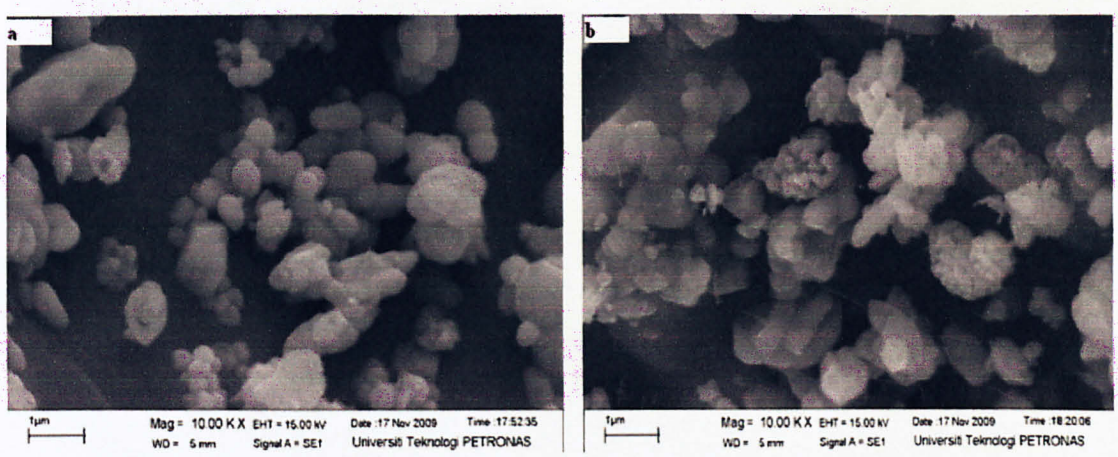

Fig 22: a)Sample 3 calcined at 400°C b) sample 3 calcined at 500°C with magnification of 10000X

Figure 22 shows that SEM image at 10000X magnification of sample 3 for both calcinations temperature 400°C and 500°C. At 500°C the author observed that, there are

some formations of rod in between the particles. The rods are form vertically towards the particles. For further clarification for the rod the author need to used FSEM while this equipment is not available at this time.

4.5 UV-VIS Spectrometer

From this UV-VIS Spectrometer test the author can test about the reflectance and absorption of the particles. Absorbance value is opposite with the reflectance value while higher absorbance value the percent reflectance is lower and vice versa. The sample being used for this test as below:

1. Cadmium Sulphate + Water + HNO3 + TEOS + Ethanol + NaOH
2. Cadmium Sulphate + Water + HNO3 + TEOS + Ethanol (no addition of NaOH)

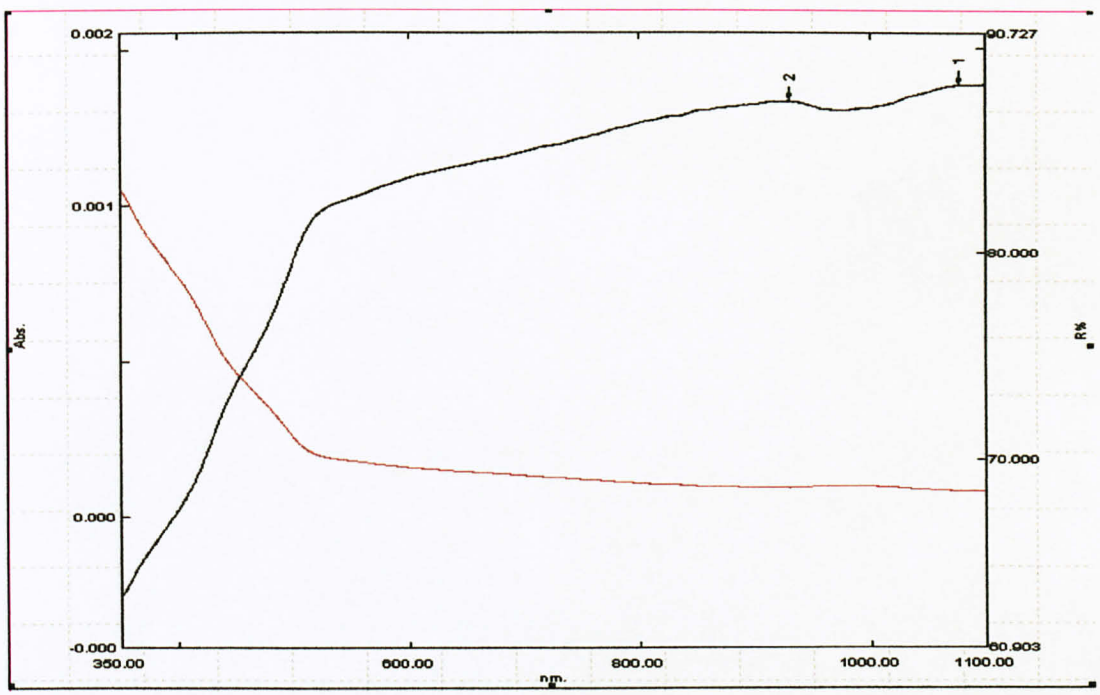

Fig 23: UV-VIS graph of absorption and reflectance of sample 1 calcined at 400°C

Table 4: Tabulated data for graph sample 1 calcine at 400°C

Peak	Wavelength	R%
1	1077.5	88.191

2	930	87.376

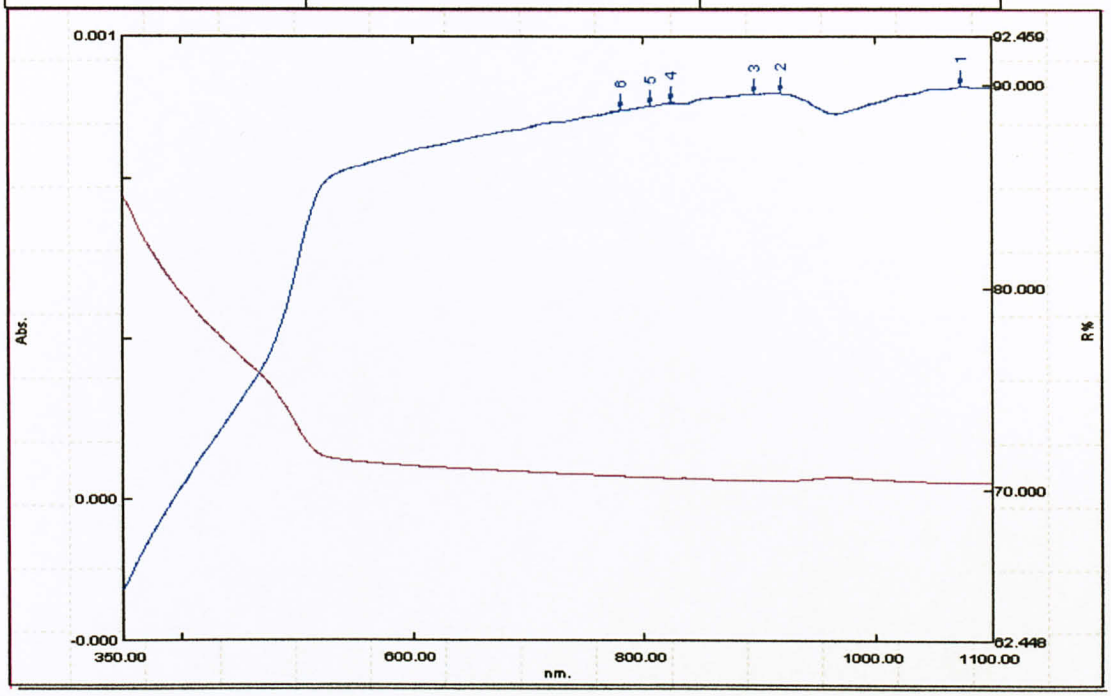

Fig 24: UV-VIS graph of absorption and reflectance of sample 1 calcined at 500°C

Table 5: Tabulated data for graph sample 1 calcine at 500°C

Peak	Wavelength	R%
1	1074.5	89.958
2	918	89.63
3	895	89.598
4	824	89.156
5	806	88.995

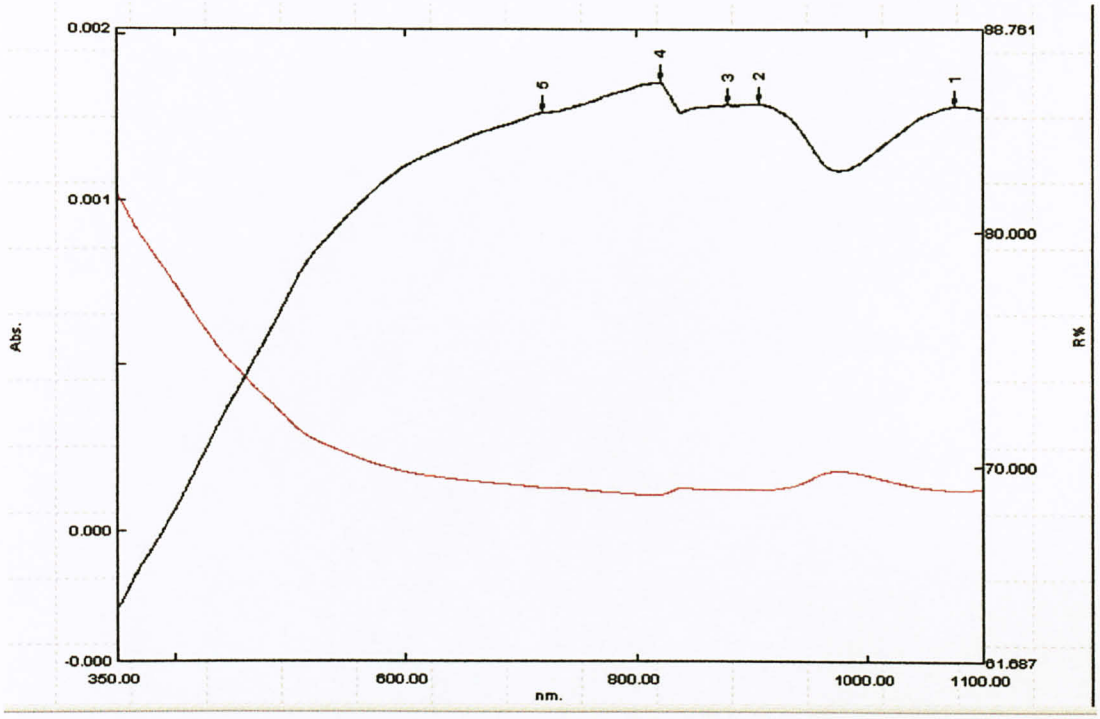

Fig 25: UV-VIS graph of absorption and reflectance of sample 2 calcined at 400°C

Table 6: Tabulated data for graph sample 2 calcine at 400°C

Peak	Wavelength	R%
1	1075.5	85.405
2	906	85.517
3	879	85.516
4	821	86.505
5	718.5	85.17

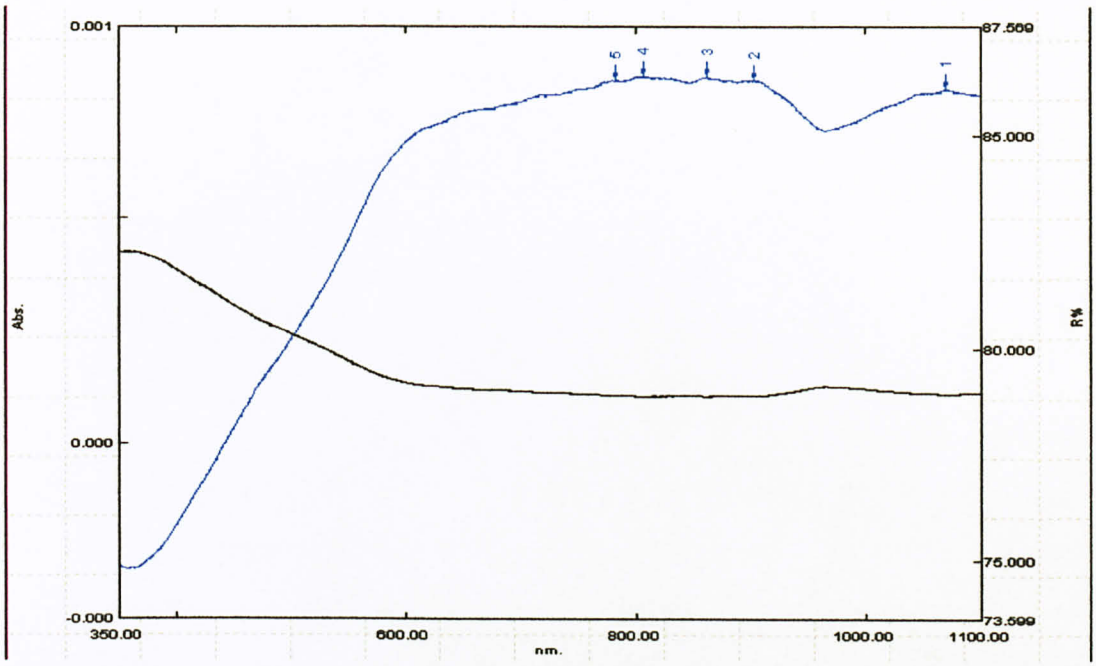

Fig 26: UV-VIS graph of absorption and reflectance of sample 2 calcined at 500°C

Table 7: Tabulated data for graph sample 2 calcine at 500°C

Peak	Wavelength	R%
1	1075.5	86.099
2	904	86.32
3	862	86.386
4	807.5	86.404
5	782.5	86.31

For sample 1 the reflectance value is differ as sample being calcined at 400°C and 500°C. At 400°C the reflectance peak is happened at 2 peaks while for 500°C the reflectance happened at 5 peaks. This is shows that as the calcinations temperature increase the reflectance peaks also increase for sample 1. This means that since the reflectance point is increase the applications also become wider for this sample since each peaks represent different value of wavelength.

While for sample 2, the reflectance value is fluctuated around 85-86% of reflection. But then the peaks at certain wavelength for both calcined temperature 400°C and 500°C is the same which are 5 peaks and the wavelength of the reflectance point is lies between 700nm – 1076nm. This is due to no addition of NaOH then the particles size is uniformly produced.

From the UV-VIS graph the absorbance value is lower for higher calcinations temperature. Lower absorbance means that lower in specific area and larger particle size.

4.6 Expected X-Ray Diffraction (XRD)

X-Ray Diffraction Analysis (XRD) is the primary tool for investigating the structure of crystalline materials, from atomic arrangement to crystallite size and imperfections. Therefore the author chose this test to investigate the structure of the crystalline final product which is CdO. Due to limiting equipment and time constraint the XRD test cannot be achieved for this time. Figure 27 shows XRD spectrum form Goshal et al, 2009, samples prepared with different amount of NaOH.

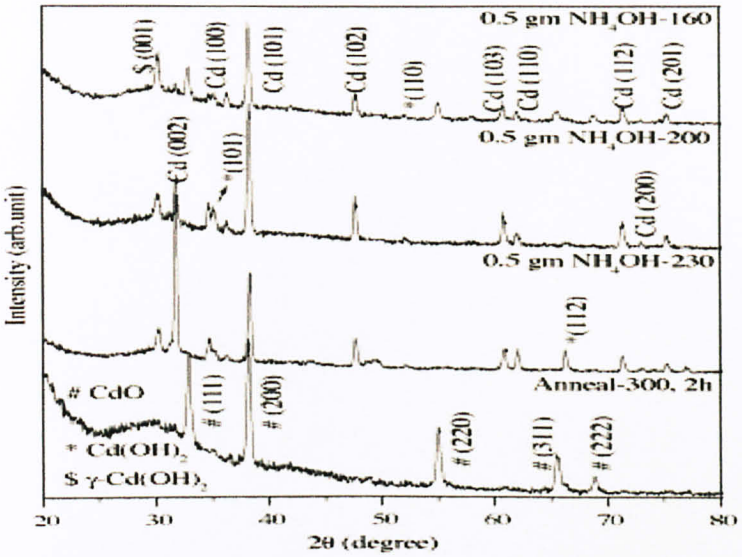

Fig 27: XRD pattern of the samples prepared with ammonium hydroxide at different temperatures (160 °C, 200 °C, 230 °C) and the sample annealed at 300 °C for 2 h. *Ghoshal et al, 2009.*

CHAPTER 4

CONCLCUSION AND RECOMMENDATIONS

4.1 CONCLUSION

The main objective of this study is the synthesis of high surface CdO nanoparticles using sol-gel method. For the initial stage, a lot of literature study being done by the author in order to achieve the objectives for the next stage. From the literature study, the author gained the main ideas of how to synthesis highly surface CdO nanoparticles using sol-gel method as well as the parameters and operating conditions for the process.

After literature study the author had finish doing the lab experiment for the sol-gel preparation as well as calcinations process for the samples. After observation made from the physical change of the calcined sample, the author precisely expect some result according to the literature study.

After lab experiment, the author had test the samples being calcined using Scanning Electron Microscopy and also using UV-VIS Spectrometer. From SEM the author can conclude that the particles produced from this experiment are with high surface area with increasing of the calcinations temperature. While for addition of Barium Nitrate there some formation of rods being observed by SEM image.

While for UV-VIS test, the author gathers the data about the absorbance and reflectance of the final products. From the test, as the absorbance value is high then the reflectance value is low and vice versa. There also different reflectance points at certain wavelength for different sample calcine at different temperature.

While doing the lab experiment, the author already made some improvement on the chemical being used for this sol-gel process. For example, usage of TEOS for sol-gel process can reduce the time taken to form gel from solution. The author also notice others parameters that will affect the formation of gel in sol-gel process such as the Ph value and etc.

4.2 RECOMMENDATION

- Use of Trimethylamine (TMA) to promote the particles growth rather the shape controller.
- Use of suitable precursor
- Thermogravimetric Analysis (TGA) need to be done in order to determine the calcinations temperature, as calcinations is the vital process in gaining the optimum final product.
- Characterization equipment should be available in lab for product testing purpose.

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